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(54) Title: METHOD AND DEVICE FOR CLEANING COMBUSTION EXHAUST GAS USING A PLASMA

(57) Abstract

The present invention relates to a method and device for cleaning of exhaust gas from a power plant burning hydrocarbon fuel including the step of letting the exhaust gas pass a cold plasma excited in a discharge chamber by creeping electric discharge at low, normal or elevated pressure of the exhaust gas. According to the invention volumetric creeping discharge is excited by a system of capacitors connected in series.

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METHOD AND DEVICE FOR CLEANING COMBUSTION EXHAUST GAS USING A PLASMA

FIELD OF INVENTION

The present invention relates to the field of ecology and more particularly, to means for conversion and destruction of unburned fuel rests and removal of toxic products of incomplete combustion from exhaust and flue gas, and especially decomposition of nitrogen oxides and carbon oxides by using plasma.

BACKGROUND OF THE INVENTION

Emission from internal combustion engines and other products of fuel combustion comprise toxic components such as nitrogen oxides (NO_x), carbon monoxide (CO), residual hydrocarbons (CH_x) and other compounds. The percentages of nitrogen oxides, carbon monoxide and residual hydrocarbons are restricted by special legislative acts, such as EURO-I, EURO-II etc.

Russian patent no. 1808096 discloses a method for removal of particulates from exhaust or flue gas, by burning them by means of air or gas enriched with air. The device for realization of this method comprises a vessel being a section of the exhaust manifold, and at least a couple of insulated electrodes, connected to a high-voltage high-frequency generator and located in the internal space of the exhaust manifold. One of said electrodes is formed as an oblong conductive body, and a portion of the internal surface of the manifold is used as, or presents, another electrode. Thus this portion of the manifold can be used as ionizer. The device also comprises an electric heater with a spark plug or glow filament for elimination of accumulated particulates. The carbon particulates entering the exhaust manifold together with exhaust gas are electrized and settled on the internal wall of the vessel. When the settled sediment reaches a predetermined thickness, a heater is activated. The heater can be formed as a resistor and/or electrodes for pulse or glow discharge. The sediment is heated to temperatures of about 700-800 K, temperatures at which carbon is inflamed. The disadvantage with the known device is that it does not provide elimination of all products formed at fuel

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combustion, e.g. such gases as carbon monoxide, nitrogen oxides and residual hydrocarbons.

U.S. Patents 4,885,140; 5,199,257 and 5,402,639 also describe the burning of soot settled on the walls of a ceramic channel or conductor. The said particulates are burned in an electric field. The separated particulates are oxidized by free ions or ions on oxygen. Drawbacks of these methods are unstable discharge conditions, and by not assuring elimination of also other impurities of exhaust gas, the cleaning efficiency is not increased.

An electric plasma discharge, ionization of a gas to a plasma, is often created by the electrical discharge appearing between two metal electrodes. The type of plasma discharge may be altered by the frequency used.

There have been some attempts to clean exhaust gas with plasma treatment, using metal electrodes and a dielectric. US Patent No. 3,983,021 discloses a process of decomposition of nitrogen oxides. The process includes extraction of nitrogen oxides from gas mixtures using solid bodies and decomposition of the nitrogen oxides by generating a dilute plasma by electric discharge. The solid bodies, being catalysts, are in the form of spheres, cylinders, granules or others, and positioned in the discharge zone in such a way that gas is subjected to action of both discharge and solid bodies. The discharge can be either of corona type (with alternating or direct current), or high-pressure glowing, radiofrequency or microwave discharge. The plasma is formed owing to discharge between two electrodes, one of which has an isolating dielectric layer on its surface. The disadvantages with this method are that only a low gas cleaning efficiency is provided because of the high hydraulic resistance of solid phase filling the reactor, and that only nitrogen oxides and not other impurities contained in exhaust gas are eliminated.

It has been found that there are good possibilities to change the composition of exhaust gases by using plasma with a temperature below 1200 K. It should be noted that it is difficult to generate a stable plasma at low temperatures. Control of certain parameters are required to keep the cold plasma.

A method by the same inventors as for the present invention is known, which is disclosed in Russian Patent No.2115062, consisting in the use of a moving, creeping discharge for cleaning of vehicle exhaust. The goal of this invention was to use a creeping discharge plasma, because it is energetically preferable to activate the plasma with a moving discharge, owing to that a creeping discharge is ignited at relatively low values of frequency and power. See definition for creeping discharge below. Toxic components of exhaust gas are afterburned or decomposed by heating to temperatures where the components goes over into ionized state. The ionization is carried out under conditions of cold plasma formation at low, normal or elevated pressure of exhaust gas, owing to both residual heat of fuel combustion and additional source of electric energy obtained by direct conversion of exhaust heat. Electrical conditions of the cold plasma formation are determined by exhaust gas composition.

For realization of the known method a portion of the manifold for gas component removal presents a discharge chamber connected to a power source and provided with a voltage transformer. At least one electrode is installed in the chamber, and the metallized internal surface of the dielectric portion of manifold is used as the second electrode. In another embodiment, a converter of heat-to-electricity is used together with the chamber, and a part of the exhaust heat is converted into electric energy and used for the ionization of the gas medium. An energy store, e.g. high-capacitance capacitor device, is installed to provide voltage sufficient for ionization of gas.

The inventors of the present invention have found out that good efficiency of cleaning impurities from exhaust gas should be achieved in the presence of a so called creeping plasma discharge, ignited volumetrically by applying stable operating parameters, of which the most important is the temperature. This creeping volumetric discharge could be explained as a large amount of sparks of discharge formed between the dielectric layers, which together with a cavity for moving gas forms an interelectrode gap. The sparks are moving vertically to and from the surfaces of dielectric, being distributed uniformly through the space, and having sizes of about 0.01-0.001 mm, thereby forming a volume of sparks in the space.

Studies accomplished by the same inventors have later shown that the device for plasma formation of RU 2.115.062 do not provide a volumetric creeping discharge. Rather the discharge of this known method is most usually ignited only restrictedly, in one part of the space for moving of gases (cavity) and can migrate along the dielectric surface without ionization of the whole gas flow. A more sophisticated arrangement of both electrodes and the dielectric portion, and of the whole device is required for the ignition of creeping discharge in the whole volume of gas flow. Furthermore, there are no means for the burning of several gas components simultaneously, the method provides only gas treatment for one gas component at each time.

The desired volumetric creeping discharge has the characteristics of controlled temperature, degree of intensity, and with controlled and equal burning conditions through the entire working volume of the discharge chamber. Neither arc discharge, corona, high-voltage spark discharge, or high-pressure glowing discharge correspond to this condition of having electrical discharge in the whole rather large volume, being stable at relatively low values of frequency and power, because of great temperature differences of plasma in zones around the electrodes, or because of the presence of high-temperature arc or spark channels. For instance, instead of decomposition generation of nitrogen oxides from N_2 of exhaust gas takes place, at the high-temperature arc or spark channels.

The formation of a stable volumetric creeping discharge plasma of controlled temperature, degree of intensity, and with controlled and equal burning conditions through the entire working volume of the discharge chamber has been solved according to the present invention. The object of the present invention is to create a method for plasma cleaning of gas formed at fuel combustion, providing considerable increase of gas cleaning efficiency especially from CO, NOx, CHx and to decrease the energy consumption.

SUMMARY OF THE INVENTION

The object of the invention is obtained by a method for cleaning of exhaust gas from a power plant burning hydrocarbon fuel including the step of letting the exhaust gas pass a cold plasma excited in a discharge chamber by creeping electric discharge at low, normal or elevated pressure of the exhaust gas, characterized in that volumetric creeping discharge is excited by a system of capacitors connected in series. Thereby a parameter controlled system for the ignition and burning of plasma, required for the gas cleaning is obtained .

In a preferred embodiment the system of capacitors consists of an array of capacitors separated from each other by a dielectric and the working cavity.

In another preferred embodiment the system of capacitors is provided with a system of resistors and these systems are created by metal filled cells in a carbide skeleton body.

In both embodiments the flow of exhaust gas is preferably made to pass at least two zones of cold plasma having different temperatures the cold plasma in the at least two zones is stabilized and in that the temperature in the respective zone is uniform and corresponds to the activation energy for dissociation and/or recombination of a certain component in the exhaust gas. The exhaust gas can be influenced by a permanent magnetic field simultaneously as the gas passes through a cold plasma.

The invention also relates to a device for cleaning of exhaust gas from a power plant burning hydrocarbon fuel comprising at least one discharge chamber having a working cavity with electrodes connected to a power source in which a cold plasma is exited in by creeping electric discharge at low, normal or elevated pressure of the exhaust gas, characterized in that the at least one discharge chamber includes a system of capacitors connected in series and in that the working cavity is surrounded by a dielectric material.

In one preferred embodiment the discharge chamber comprises conductive sections insulated from each other and from the electrodes and placed in such a way that

electrodes and the sections together with the dielectric and the working cavity form a system of capacitors connected in series. The thickness of the insulator between the electrode and the conductive sections is 5-8% of the interelectrode gap and the conductive sections are made in the form of plates.

In another preferred embodiment the system of capacitors is provided with a system of resistors, the electrodes of the chamber being formed of metal filled cells of a cellcontaining carbide body, wherewith the metal of the carbide is selected from the IV, V or VI group of the Periodic system, and the metal is chosen from the group including Cu, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and/or W. Preferably, the electrodes are made of a composite material comprising chromium carbide and copper.

The discharge chamber is additionally provided with a current limiter made in the form of a capacitor connected in series with the chamber and a power source. The capacitances of the discharge chamber and the current limiter of the discharge chamber have the following dependence: $C_{cl} \geq 10\ C_c$ where C_c is the capacitance of the discharge chamber, and C_{cl} is the capacitance of the current limiter. The device can comprise two or more discharge chambers forming a group of discharge chambers, the discharge chambers in the group being connected in parallel with one another in the gas flow, whereby the group of chambers is additionally provided with a current limiter in the form of a capacitor connected in series with the current limiter of each chamber of the group and with a power source. The reactive power of the current limiter of the group of discharge chambers is 5 – 15 times as high as the reactive power of the current limiter of each discharge chamber.

Advantageously, the device comprises at least two discharge chambers or groups of discharge chambers installed along the gas flow and the flow section of a discharge chamber or a group of discharge chambers is chosen proceeding from the condition of having a constant hydraulic resistance for the gas flow. Furthermore, the surface of the working chamber is made of an ablating material, such as oxide-nitride ceramics of the $BN\text{-}SiO_2$ system.

Permanent magnets or electromagnets can be mounted/placed in such a way that their lines of force pierce the at least one discharge chamber being in the same or opposite directions to each other and the device can additionally comprise a heat-to-electricity converter and an electric energy store.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described with reference to the enclosed figures, of which,

Fig.1 presents schematically the entire afterburning and decomposition system,

Fig.2 presents a section of the device being a part of manifold

Fig.3 presents one embodiment of the gas discharge chambers with electrodes made of metal,

Fig.4 presents a circuit diagram of the gas discharge chamber with electrodes made of metal,

Fig.5 presents a chamber with electromagnets,

Fig.6 presents a gas discharge chamber with electrodes made of composite material, and

Fig.7 presents a circuit diagram of the gas discharge chamber with electrodes of composite material.

DESCRIPTION OF THE INVENTION

The technology of the present invention is characterized in the use of cold plasma, formed by a creeping volumetric type of discharge, that allows to realize the cleaning of a

multicomponent exhaust gas at relatively low-energy and consequently at low-temperature conditions. This is especially of importance for the conversion/destruction and removal of nitrogen oxides that can at high temperatures be reformed from nitrogen residues.

It is an object of the present invention to increase the degree of gas cleaning, by the formation of a stable volumetric creeping discharge in a gas flow volume surrounded by dielectric, wherein the characteristics of said discharge can be altered deliberately to provide and optimise a selective destruction/removal (afterburning and decomposition) of predetermined components of exhaust gas, such as CO, NO_x, CH_x. These toxic components of exhaust gas are afterburned or decomposed by heating to temperatures where almost all of the gas components goes over into ionized or excited state. The ionization is carried out under conditions of cold plasma formation at low, normal or elevated pressure of exhaust gas. Thus the cold plasma that is formed in the discharge chamber(s), is being a mixture of ions, electrons and molecules.

The essence of the present invention consists in, that in the method of cleaning of exhaust gas from the burning of hydrocarbon fuel by the means of cold plasma, excited by a creeping electric discharge, the plasma is being of controlled temperature, and exited by a volumetric discharge either in;

(1) a single discharge chamber (reaction chamber), with a single volume of gas flow in the working cavity surrounded with dielectric; or

(2) several discharge chambers, with several volumes of gas flow. In this case the gas flow volumes are produced by dividing the flow into several by leading the flow into different discharge chambers. The discharge chambers are united in groups, and in each of them a volumetric creeping discharge with equal characteristics is exited. In such way the whole gas flow is subjected by discharge of constant parameters.

To solve the problems with the instability of the creeping discharge on the surface of dielectric, and instead to produce a volumetric creeping discharge through the entire volume of gas flow in the discharge chamber(s) through a system of capacitors connected in series, the discharge chamber(s) are made according to two alternative embodiments,

(a) by having two layers of conductive elements (metal electrodes) being separated by a dielectric and a gas cavity, and two inner layers formed by conductive sections, isolated from each other and from the electrodes,

(b) by having conductive elements (electrodes) being made of a refractory composite material, the composite comprising of materials having different conductivity, e.g. of a chromium carbide skeleton surrounded with copper. These materials having different conductivity are forming a cell-like structure.In this embodiment there are no conductive inner layers.

In the first embodiment, the metal electrodes and the dielectric layer with working cavity forms an electric capacitor. The capacitance of this capacitor can be quantitatively adjusted by selection of the dielectric layer thickness and correlation between the areas of the two conductive element layers, i.e. the metal electrode and the conductive sections. The quantitative value of this capacitance is determined by the capacitance of another capacitor, this capacitor being formed by the additional conductive sections and the dielectric and the discharge capacitance formed by additional conductive sections, the dielectric and the gas cavity.

The correlation between these two capacitances is determined proceeding from desirable discharge chamber performance and the necessity of compensation for manufacturing errors of the discharge chamber components, regarding their dimensions, surface smoothness and if the surfaces are parallel. Matching of the capacitance of the capacitors for volumetric plasma formation is simplified.

According to the other embodiment, the electrodes consisting of a refractory composite material gives a discharge of the whole area, compared to ordinary metal surfaces that often has defects leading to a concentration of the discharge formation to these defects.

Variation of the discharge parameters in various discharge chambers or groups of discharge chambers, assures the selective destruction and removal (by decomposition and afterburning) of gas components in the flow, where each discharge chamber or group of

discharge chambers is intended for the removal of a specific gas component, thus substantially increasing the efficiency of cleaning.

The very important parameter is the control of the temperature field of the volumetric cold plasma discharge in the discharge chamber. The optimum rates for the reactions of destruction or conversion for various gas components are different. Thus for each gas component certain temperature ranges must be achieved. These temperature ranges are partly obtained by thermodynamical calculations and partly by experiments.

It has been established that afterburning of carbon monoxide (CO) into carbon dioxide (CO_2) begins at temperatures of $T \geq 800$ K and is accelerated considerably by presence of water vapour at temperatures of $T \geq 1400$ K.

According to thermodynamical calculations the temperature range 1600-1800K is favourable for decomposition of nitrogen oxides. The reverse process, formation of nitrogen oxides, begins at $T \geq 3000$ K with equilibrium at $T = 4000$ K at the level of 5% NO; which corresponds with published data by Ya.B.Zeldovich et al., Oxidation of nitrogen at burning, //AN SSSR Publishers, 1947.

The complicity of the proceeding of the reactions must be taken into account, and especially concerning the resonance character of reaction in cold plasma. It is known, for instance, that the initiation of the afterburning of CO into CO_2 requires a different activation energy than for the complex chain reactions of NO_x recombination, such as

$$NO \begin{cases} + N \text{ -------> } | \ N_2 + O \\ + O \text{ -------> } NO_2 \end{cases}$$

And

$$NO_2 \begin{cases} + N \text{ -------> } N_2O + O \\ + OH \text{------> } HNO_3 \\ + O \text{ -------> } NO + O_2 \end{cases}$$

For carbon monoxide the following reactions can be characterised by:

T < 800 K: $2CO \text{ -----> } O_2 + C$

T > 1600 K: $CO_2 \text{ -----> } 2CO + O_2$

$H_2O \text{ -----> } H + OH$

$2OH + CO \text{ ---> } CO_2 + H_2$

In the method of the present invention, the process of afterburning of gas components into cold plasma is carried out at low, normal or elevated pressure of exhaust gas with means of both residual heat of fuel combustion and additional electrical energy obtained by direct conversion of waste-gas heat into electrical energy.

The electrical conditions of cold plasma formation depend on the gas composition, i.e. on the impurities (NO_x, CO etc.) that are to be eliminated in the given reaction chamber or group of reaction chambers. The best results have been obtained in cold plasma formed at operation voltages in the range of 1500-3000 V, frequencies 18-20 kHz and electric power supply 0.05-0.35 kVA. For stabilization of the electron and ionic flows in the discharge chambers external magnetic or electromagnetic field is used, which increases the total efficiency of the method.

The gas cleaning device with at least one discharge chamber or several discharge chambers are able to transform current from an external source into high-frequency (18-20 kHz) and high-voltage (up to 3000V) current for the formation of electric discharge between the electrodes.

In most known inventions attempt is made to apply ordinary electric discharges, as in standard spark plugs for automotive engines, at voltage of some ten kV on the metal electrodes. In the present invention a voltage by an order lower is used and the discharge is formed not on the metal (the metal electrode, or alternatively the conductive part of the composite electrode), but on a the dielectric, separating the electrodes from the toxic corrosive gas in the discharge chamber.

The flow sections, formed by the working cavities of the discharge chamber or group of discharge chambers, are made proceeding from the conditions, i) of minimizing the hydraulic resistance for the gas flow, thus avoiding decrease in the performance of the device producing the gas flow, e.g. of the engine, and also ii) assuring necessary flow rate and residence time of the gas in the discharge chamber giving the best degree of cleaning of the gas.

To assure selective cleaning of exhaust gas, i.e. selective destruction and removal of different exhaust gas components, the discharge chambers or groups of discharge chambers, are positioned along the gas flow. Further, in each of them, or in each group, conditions necessary for the excitation of discharge providing selective dissociation and/or recombination of a certain component are created.

For easier optimisation of the cold plasma temperature for certain reactions current limiting capacitors are included in the device. Each discharge chamber is provided with a current limiter in the form of a capacitor and also each group of chambers is provided with a current limiter in the form of a capacitor, which assures simultaneous ignition of plasma in all chambers and uniform burning of the plasma. The single chamber current limiter is connected in series with the chamber and power source, whereas the current limiters of the multi-chamber groups are connected in series with the current limiters of each single chamber and power source.

The optimum conditions for ignition of plasma and uniform burning of the discharge are the following:

- the thickness of the insulator between the electrode and the conductive sections is approximately 5-8% of the interelectrode gap formed by the working cavity and the dielectric;
- the capacitances of the discharge chamber(s) and the current limiters of the chamber(s) should preferably have the following relationship:

$$C_{cl} \geq 10\, C_c \qquad (1)$$

where C_c is the discharge chamber capacitance, and C_{cl} is the current limiter capacitance.

The system of current limiting capacitors connected with the discharge chambers, allows to create identical conditions for discharge burning. The capacitance of each capacitor in the system given by the relationship (1) is obtained experimentally.

The groups of chambers are connected to the power source through current limiters, having a reactive power 5-15 times greater than the reactive power of the discharge chamber current limiters, corresponding to the energy consumption sufficient for the decomposition of one or several of the gas impurities.

In the embodiment using metal electrodes, the device for realization of the claimed method comprises at least one discharge chamber being formed by a capacitor with plate electrodes and where the interelectrode gap is formed by the working cavity and dielectric. For the stabilization of the discharge that is excited, the device is provided with additional conductive sections, insulated from each other and from electrodes, and installed at dielectric in such a way that they together with the dielectric and working cavity, form a system of capacitors connected in series.

In one of the embodiment using metal electrodes, the additional conductive sections (that are placed on the chamber-facing dielectric surface) consist of 0.05-0.1 mm thick Mica inserts, and insulated titanium cells of 3-5 μm thick have been sprayed in vacuum onto the Mica inserts. The total area of the titanium sections, that have been sprayed through a mask, is being less than the area of the metal electrode. The metal electrodes may be made of e.g. of steel, copper or brass.

This concept is provides a system of small capacitors formed by the titanium sections together with the dielectric and the gas gap (flow section), i.e. cells. These cells have as good as uniform conditions for plasma ignition, for the unification of the conditions for discharge formation and for the levelling of possible variation in dimensions of electrodes, at manufacturing of electrodes and dielectric, and surface defects at them.

These good and uniform conditions of plasma assures the increase of the total volume filled with plasma and the absence of plasma-free volumes in the discharge chambers, through which uncleaned gas flow could pass.

In one of the alternative embodiments to achieve uniform volumetric burning of discharge in the chamber, the electrodes are made of a refractory composite material comprising at least one metal carbide and at least one metal. The composite material has a cell-like structure due to the presence of a low conductive metal carbide phase and a high conductive metal phase. The metal phase on the surface of two opposite electrodes forms with the dielectric and the working cavity a system of discharge capacitors connected in series. The cell boundaries and the metal carbide will here form a system of resistors, which is connected to the system of capacitors.

In this embodiment the conductive sections located at the dielectric forming a system of capacitors (as in the other alternative embodiment) are unnecessary.

The said refractory composite material comprises a at least one carbide of a metal, said metal chosen from the group of IV, V or VI group of Periodic system, and at least a metal chosen from the group of Cu, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and/or W. The most preferred refractory composite comprises Cr_2C_3 and Cu. The preferred composite material is made according to the method of the PCT application PCT/EP97/011566.

To increase the durability of the device, the surface of the dielectric of the working cavity is coated with ablating material, such as oxide-nitride ceramics. The ablating insulator materials used are stable, having high thermal chock resistance and being inert towards carbon and soot. Thereby there is no conductive film of deposited carbon formed on the surface.

The device can be equipped with a source of magnetic field, assuring the formation of a magnetic field in the interelectrode gap of the discharge chamber. The said source of magnetic field is either,

- a number of electromagnetic coils located at both end faces of the discharge chambers, or surrounding the discharge chambers along its entire length, or
- permanent magnets, inserted into the discharge chambers and placed behind each electrode,

creating a magnetic field of a certain magnitude at the dielectric surface to increase the efficiency of the process. The residence time of the ionized components of gas in the discharge chamber can be increased by the action of these magnetic fields.

The essence of the invention is illustrated with the Figures 1, 2, 3, 4, 5, 6, and 7:

Figure 1 presents schematically the entire system for the afterburning and decomposition of emission components according to the present invention.

Figure 2 presents a section of the device being a part of the manifold.

Figure 3 presents one embodiment of the gas discharge chambers with electrodes made of metal.

Figure 4 shows a circuit diagram of the discharge chamber with electrodes made of metal.

Figure 5 shows a reactor with electromagnets.

Figure 6 shows a discharge chamber with electrodes made of a refractory composite material.

Figure 7 shows a circuit diagram of the discharge chamber with electrodes of a refractory composite material.

Fig. 1 shows the afterburning and decomposition system according to the present invention comprises a piping 1 (exhaust manifold) connected with a combustion chamber (not shown in the figure), a thermoemission converter of heat into electricity 2, an energy store 3, a voltage transformer 4, and the gas cleaning device 5.

Fig.2 shows the gas cleaning device 5, which is formed by at least one discharge chamber 6, where the actual reactions of the removal of hazardous components of the gas flow takes place, presenting a system of capacitors with capacitance C_e formed by electrodes 7, connected through chamber current limiters 8 to a power source 9.

The chamber current limiter 8, is a capacitor (with constant capacitance irrespective of the operation conditions) of some 1000 pF for operation voltage of about 500 V, and the capacitance of current limiter 8 is at least 10 times greater than the capacitance of the discharge chamber(s) 6.

As can be seen in Fig. 2, several discharge chambers 6 form groups I, II ... etc, here an embodiment with two groups of discharge chambers (group I and group II). Each group is connected to a power source 9 through power regulators i.e. current limiters 10, that assures supply of electric power corresponding, for example to the required value for afterburning of CO or decomposition of NO_x.

In spite of similar design, the current limiters 10 and 8 have different functions. The current limiters 10 assure predetermined levels of current and voltage in the groups (I, II, ...etc.) of discharge chambers 6. In principle these are different for different reaction processes. The chamber current limiters 8, on the contrary, assure similar parameters (current and voltage) in every chamber of the group and similar conditions of the burning of discharge in parallel discharge chambers 6 of the group.

For cleaning of flows the chambers 6 are mutually connected in parallel in groups, and positioned along the gas flow. The amount of chambers in the groups and amount of said groups depend on the gas volume, rate of the gas flow, and quantity of toxic components to be burned.

Fig. 3. For this purpose electrodes 7 have been designed comprising a group of conductive sections, conductive plates 11, insulated from each other with a dielectric layer 12. The discharge chamber 6 formed by dielectrics 13, has a working cavity 14, and is equipped with electrodes (metal plates) 7. The metal plates 7 are,connected with a leader of current 15, to give voltage to the electrodes, and supplied to the discharge chamber 6.

The area of the electrodes 7 is determined experimentally and is depending on the emission gas flow rate to assure that the residence time of the gas in the discharge zone is

sufficient for complete decomposition or afterburning of a certain emission component. The area of the sections 11 is about 90 % of the area of plate 7. The dielectric gap between the electrode 7 and the plates 11 is 5-8 % of the gap between sections 11 formed by the dielectric 13 and the working cavity 14.

Fig. 4 shows a circuit diagram of the chamber 6, presenting a system of feed-through capacitors 16 (for which conductive sections 11 together with dielectric 13 presents the discharge gap) at both sides of the chamber 6 with working cavity 14 and a system of discharge capacitors 18 (for which conductive sections 11 are plates, and the working cavity 14 together with dielectric 13 is the gap).

As seen in figure 3, the chambers can be equipped with permanent magnets 17, positioned in such a manner that their magnetic lines of force are directed contrarily or similarly to each other.

Figure 5 shows a general view of the discharge chamber 6 equipped with electromagnets 19, which can also (like in the case of the permanent magnets) be installed with lines of force with the same or opposite direction to each other.

When the electrodes 7 are made of a refractory composite material, e.g. of Cr_2C_3-Cu, a circuit diagram of the chamber 6 is presented by feed-through capacitors 20 and resistors R_{BH}.

The arrangement of the discharge chamber 6 has the form as shown in Figure 6, where 15 is the leader of current, 7 the electrodes manufactured of the refractory composite material interacting with the gas through the dielectric 13 and the working cavity 14.

Figure 7 presents in a circuit diagram discharge chamber 6, with a system of discharge capacitors 20 and resistors $R_{BH,}$ where the electrodes are made of composite material.

It should be noted that the optimum conditions for burning of discharge in the discharge chambers 6 are established experimentally and selected taking into account the

dependence (1) and the size of the dielectric interelectrode gap, with the chamber capacitance C_c being as follows:

$$C_c = \sum_{i=1}^{i=n} C_{fi} + \sum_{i=1}^{i=n} C_{di} \qquad (2)$$

where C_{fi} - capacitance of feed-through capacitor of i-th discharge chamber;

C_{di} - capacitance of discharge capacitor of i-th discharge chamber.

When meeting the said conditions, the reactance X_f of the feed-through capacitor is connected with the reactance X_d of the discharge capacitor by the following dependence:

$$X_d > X_f \qquad (3)$$

This allows to create the necessary conditions for levelling the discharge at the surface of dielectric 13.

The two alternative embodiments using different electrode material have different advantages:

In the embodiment with refractory composite electrodes uniform conditions for discharge through the whole space of discharge chamber are achieved owing to the inner structure of the material, which simplifies the design of the device, but there might be some voltage losses in this case.

However, it must be noted that in embodiments with conductive sections forming a system of capacitors there are no active losses on the electrodes. Following the dependence (1) make possible to use the current limiters 8 as resistors and to control the discharge ignition and distribution in the discharge chambers 6 without active losses. The system of current limiters 8 creates similar conditions for discharge burning in the chambers 6 of each group. Thus, if a great current flows in one of the chambers 6 and the discharge is ignited, then the voltage decreases in the current limiter 8 of said chamber,

causing an voltage increase at the current limiters 8 of the other chambers of the same group, and accordingly discharge ignition therein.

The same principle as described above is used for creation of uniform distribution of discharge through chamber by means of the capacitor system, formed by sections 11 and metal electrodes 7 (feed-through capacitors 16 and discharge ones 18) in the embodiment with electrodes 7 made of metal.

The current limiters 10 also function as resistive elements without active losses.

The number of chamber groups I, II... is to be chosen depending on the number of impurities which are to be removed: two groups are needed for burning NO_x and CO simultaneously in the flow etc. The number of discharge chambers 6 in each group is chosen proceeding from the necessity of free gas flow without additional hydraulic resistance. The total area of the gas gaps must correspond to the flow area of the exhaust manifold 1, or exceed it if it is necessary to increase the residence time for the flow in the discharge chamber(s).

The device of the present invention functions as follows. The exhaust gas passes the piping 1 (e.g. being an exhaust manifold of an engine) and enters the discharge chamber 6 where the afterburning or decomposition of the exhaust gas takes place by volumetric creeping discharge formation. By means of power regulator 10 necessary power is created in chambers 6 for afterburning of, for example, CO (0.1-1.5 kVA). A magnetic field is used to increase the residence time of the ionized components of gas in the discharge chamber and to steer the motion of the electrons formed by the ionization.

EXAMPLE:

The invention is realized in a device with two chamber groups. In one of the groups comprising 21 chambers, the discharge chambers are destined for the afterburning of CO. The other group comprising 11 chambers, is destined for the decomposition of NO_x. Pyrex glass is used as dielectric.

The gas cleaning device with the said two groups of discharge chambers was placed into an exhaust manifold of a diesel engine with power of about 5 kW tested in The Diesel R&D Institute in St.Petersburg, Russia. An alternating voltage generator for 20 kHz UZU-0.25 was used as a power source.

Maximum possible parameters used for the specific equipment:
for CO-afterburning group of chambers: $C \approx 1000$ pF, $U \leq 5000$ V, $I \leq 0.1$ A;
for NO_x-decomposition group of chambers: $C \approx 235$ pF, $U \leq 4000$ V, $I \leq 0.1$ A.

The discharge chambers for NO_x-decomposition with conductive sections obtained by vacuum spraying of about a 3 μm thick titanium layer on 0.5 mm thick mica inserts and copper electrodes of were used for one series of test, and the discharge chambers for NO_x-decomposition with electrodes made of refractory composite Cr_2C_3-Cu, for another series of the test. In both series of the test the discharge chambers for CO were used with conductive sections obtained by vacuum spraying of about a 3 μm thick titanium layer on 0.5 mm thick mica inserts and copper electrodes.

During the operation of each group of chambers the engine torque was 20 Nm, and the NO_x emission was about 350 ppm.

The composition of the exhaust gas at the device outlet is analyzed by the following methods:

1) The NO_x content is determined by the method based on interaction of nitrite-ion and n-aminobenzolsulphoacid (sulphanile acid) with formation of diazo-compound which, reacting with 1-naphtylamine, gives azo dye tinting solution pale-pink to red-violet. The intensity of colour is proportional to the concentration of nitrogen oxides and is measured by a photocolorimetry method.

[Ref.: "Photocalorimetric method using Griss Iosval's reagent for determination of the concentration of nitrogen oxides": Collected methods for determination of pollutants in industrial emissions, Leningrad, Hydrometeoizdat Publishers, 1987, p.33].

2) The CO content is determined by means of an infrared gas analyzer GAI-1 API 2.840.024 destined for automatic determination of carbon monoxide content in exhaust from automotive carburetor engines, [GOST 15150-69, GOST 12997-76]. The CO content is determined by the difference of the absorption of infrared rays by the analyzed component in comparison with a reference gas cell.

Note: GOST is the State Standard System used in the Russian Federation.

At afterburning of a gas mixture containing NO_x= 0.01-0.001 wt-% and CO=1.0-1.2 wt-% there was obtained at the outlet NO_x= 0.005-0.0005 wt-%, and CO = 0.2-0.3 wt-% when using chambers with a system of capacitors (sectionalized electrodes) connected in series. Thus, the achieved decrease in NO_x content was 55-65%.

When using chambers with refractory composite electrodes the decrease in NO_x was 45-55%. After improvement and adjustment of the technology for composite electrodes manufacture these results can be enhanced. Note that the design of the discharge chambers with refractory composite electrodes is substantially simpler than with additionally introduced sectionalized electrodes.

Tests of discharge chambers with ablative oxide-nitride ceramics of the BN-SiO_2 system developed in Central Research Institute of Materials (CRIM), in St.Petersburg, Russia, have shown that there is practically no soot deposited at the discharge chamber walls, and the wear of insulation does not exceed 1 μm during 50 hours of operation, thus assuring a service life of the device of at least 100,000 hours.

Comparing the results, at gas cleaning by means of a prior art device described in RU patent 1808096 the energy consumption is about 30% higher and the cleaning degree of the engine exhaust is 5-6 times lower with regard to CO and NOx for the prior art device.

When using a thermoemission converter 2 a part of the thermal energy of the gas flow is transformed into electrical energy, which can be stored in store 3 and then transformed into high (up to 5 kV) and high-frequency (21 kHz) voltage in the transducer 4. An

additional power source can be used, in which case the voltage transducer is necessary and the energy store can be omitted.

Instruments necessary for realization of the invention are known from the state of the art. As energy store 3 a capacitor device can be used, as voltage transformer 4 - e.g. a transistor transformer. Thermoemission heat-to-electricity converter 2 can present e.g. a device in which molybdenum cathode and anode cylinders are placed coaxially with narrow interelectrode space filled with caesium vapour. Cathode cylinder emits electrons under action of heat while anode cylinder receives the electrons forming a closed circuit for load, see "Collected papers by Soviet Scientists at 11th International Conference on thermoemission conversion of energy", Moscow, VNIIT, 1969, p. 299, and 320. When connecting the ionizer 5 to an additional power source (e.g. vehicle accumulator battery) the voltage transformer 4 is necessary, while the store 3 is not needed any more. As chamber current limiters capacitors KCO can be used or any other capacitors assuring necessary capacitance at voltages 500-1000 V, e.g. K73, MBGO etc. As current limiters for group of chambers any capacitor designed for great currents and voltages above 750 V can be used. Such capacitors comprise, for example, metal plates and dielectric - paraffin, paraffin paper, transformer oil etc. The inventors used the capacitor K75-40.

Note: K73, MBGO, and K75-40 are Russian trade names.

As a summary, the claimed device allows to:

- effectively clean exhaust gas from the following components CO, NO_x, and CH_x;
- considerably increase the gas cleaning efficiency and to decrease the energy consumption owing to elimination of active losses in the system, and the creation of a self-controlled system for ignition and burning of volumetric creeping discharge;
- increase the service life of a cleaning system since the discharge occurs on the surface of dielectric and, when using oxide or other thermodynamically balanced dielectrics, the maximum time of exploitation in a gas discharge cold plasma is achieved. The maximum durability is not possible when using metal electrodes as in the known concepts.

The present invention aims to create a clean environment and can be used both in vehicles and any other fuel combustion systems without use of expensive catalysts.

CLAIMS

1. A method for cleaning of exhaust gas from a power plant burning hydrocarbon fuel including the step of letting the exhaust gas pass a cold plasma excited in a discharge chamber by creeping electric discharge at low, normal or elevated pressure of the exhaust gas, **characterized in** that volumetric creeping discharge is excited by a system of capacitors connected in series.

2. The method according to Claim 1, **characterized in** that the system of capacitors consists of an array of capacitors separated from each other by a dielectric and the working cavity.

3. The method according to Claim 1, **characterized in** that the system of capacitors is provided with a system of resistors.

4. The method according to Claim 3, **characterized in** that the system of capacitors and resistors consists of metal filled cells in a carbide skeleton body.

5. The method according to any of claims 1-4, **characterized in** that the flow of exhaust gas is made to pass at least two zones of cold plasma having different temperatures.

6. The method according to Claim 5, **characterized in** that the cold plasma in the at least two zones is stabilized and in that the temperature in the respective zone is uniform and corresponds to the activation energy for dissociation and/or recombination of a certain component in the exhaust gas.

7. The method according to any of claims 1-6, **characterized in** that the exhaust gas is influenced by a permanent magnetic field simultaneously as the gas passes through a cold plasma.

8. A device for cleaning of exhaust gas from a power plant burning hydrocarbon fuel comprising at least one discharge chamber having a working cavity with electrodes

connected to a power source in which a cold plasma is exited in by creeping electric discharge at low, normal or elevated pressure of the exhaust gas, **characterized in** that the at least one discharge chamber includes a system of capacitors connected in series and in that the working cavity is surrounded by a dielectric material.

9. The device according to Claim 8, **characterized in** that in the discharge chamber further comprises conductive sections insulated from each other and from the electrodes and placed in such a way that electrodes and the sections together with the dielectric and the working cavity form a system of capacitors connected in series.

10. The device according to Claim 9, **characterized in** that thickness of the insulator between the electrode and the conductive sections is 5-8% of the interelectrode gap.

11. The device according to Claim 9 or 10, **characterized in** that the conductive sections are made in the form of plates.

12. The method according to Claim 8, **characterized in** that the system of capacitors is provided with a system of resistors

13. The device according to Claim 12, **characterized in** that the electrodes of the chamber are formed of metal filled cells of a cellcontaining carbide body.

14. The device according to Claims 12-13, **characterized in** that the metal of the carbide is selected from the IV, V or VI group of the Periodic system, and the metal is chosen from the group including Cu, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and/or W.

15. The device according to Claims 12-14, **characterized in** that the electrodes are made of a composite material comprising chromium carbide and copper.

16. The device according to any of Claims 8-15, **characterized in** that the discharge chamber is additionally provided with a current limiter made in the form of a capacitor connected in series with the chamber and a power source.

17. The device according to Claim 16, **characterized in** that the capacitances of the discharge chamber and the current limiter of the discharge chamber have the following dependence: $C_{cl} \geq 10\ C_c$ where
C_c is the capacitance of the discharge chamber, and C_{cl} is the capacitance of the current limiter.

18. The device according to any of Claims 8 – 17, **characterized in** that it comprises two or more discharge chambers forming a group of discharge chambers, the discharge chambers in the group being connected in parallel with one another in the gas flow.

19. The device according to Claim 18, **characterized in** that the group of chambers is additionally provided with a current limiter in the form of a capacitor connected in series with the current limiter of each chamber of the group and with a power source.

20. The device according to Claim 19, **characterized in** that the reactive power of the current limiter of the group of discharge chambers is 5 – 15 times as high as the reactive power of the current limiter of each discharge chamber.

21. The device according to any of Claims 8– 20, **characterized in** that it comprises at least two discharge chambers or groups of discharge chambers installed along the gas flow.

22. The device according to any of Claims 8- 21, **characterized in** that the flow section of a discharge chamber or a group of discharge chambers is chosen proceeding from the condition of having a constant hydraulic resistance for the gas flow.

23. The device according to any of Claims 8 – 22, **characterized in** that the surface of the working chamber is made of an ablating material.

24. The device according to Claim 23, **characterized in** that the surface of the working chamber is made of oxide-nitride ceramics of the BN-SiO_2 system.

25. The device according to any of Claims 8–24, **characterized in** that it comprises permanent magnets mounted/placed in such a way that their lines of force pierce the at least one discharge chamber being in the same or opposite directions to each other.

26. The device according to any of Claims 8–24, **characterized in** that it comprises additionally electromagnets mounted/placed in such a way that their lines of force pierce at the least one discharge chamber being in the same or opposite directions to each other.

27. The device according to any of Claims 8–26, **characterized in** that it comprises additionally a heat-to-electricity converter.

28. The device according to Claim 27, characterized in that it comprises additionally an electric energy store.

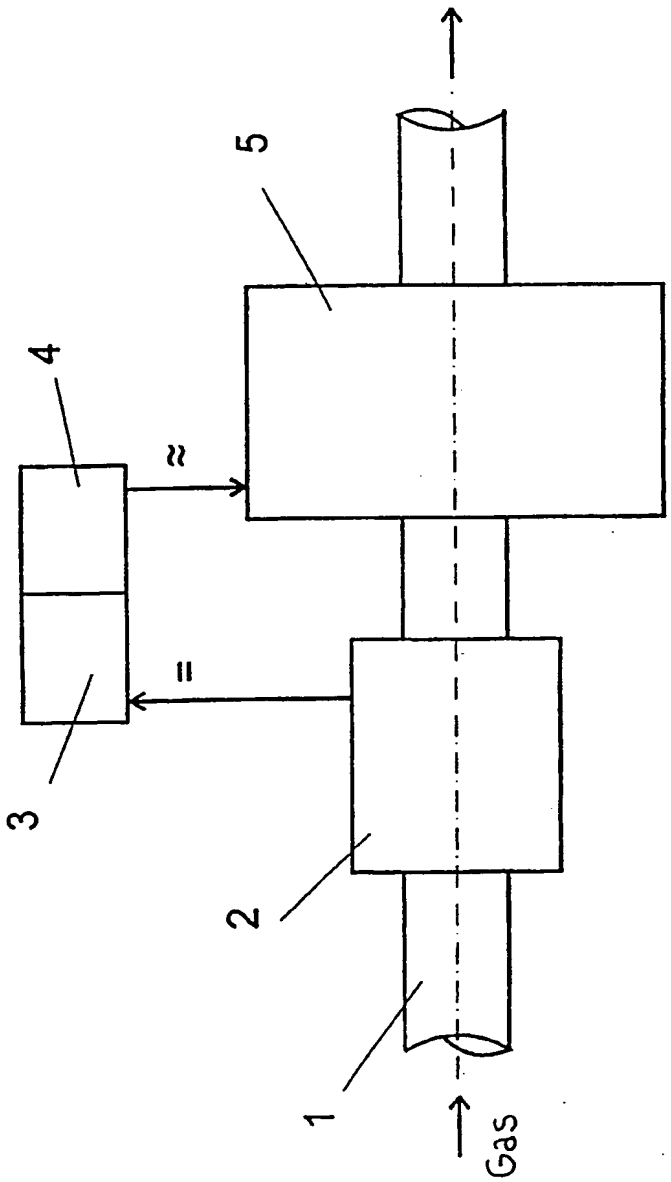

FIG.1

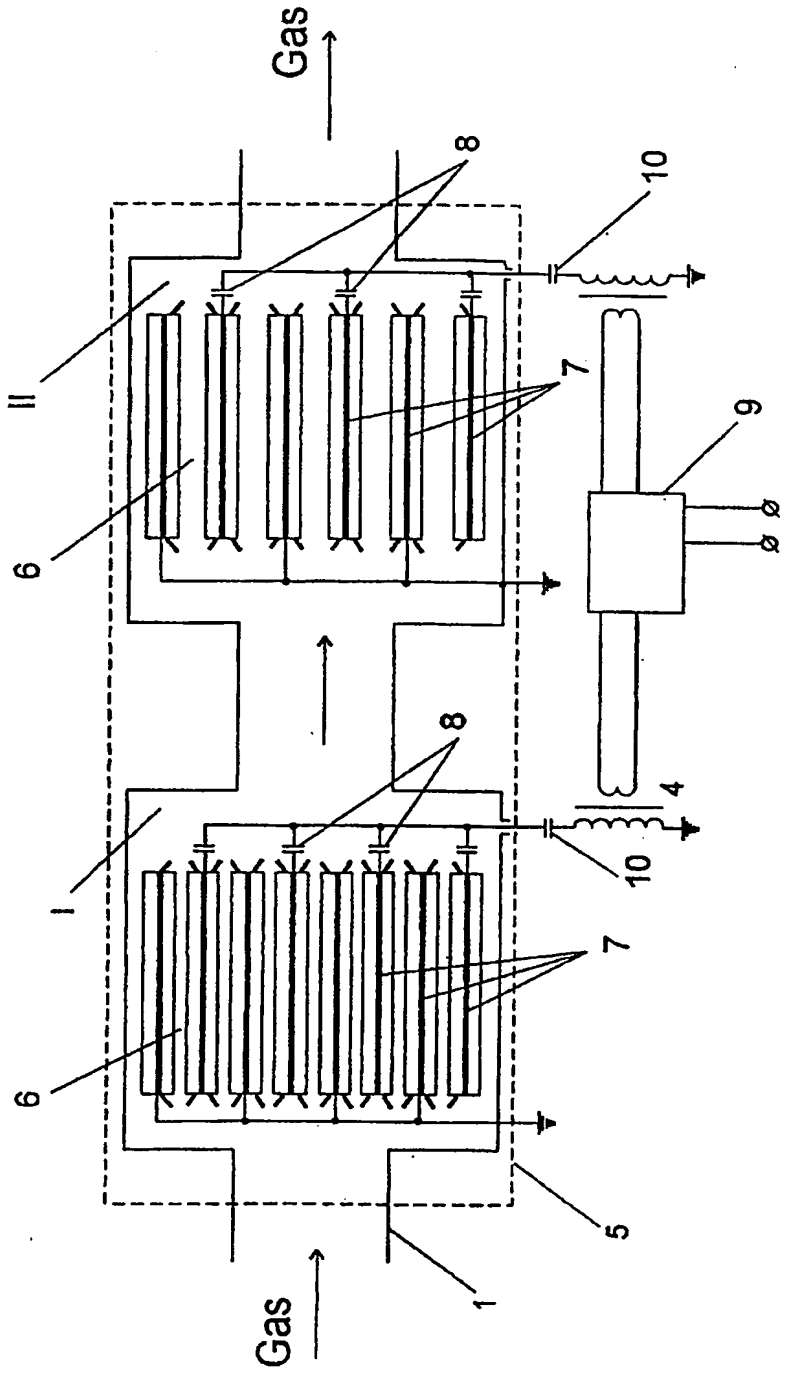

FIG.2

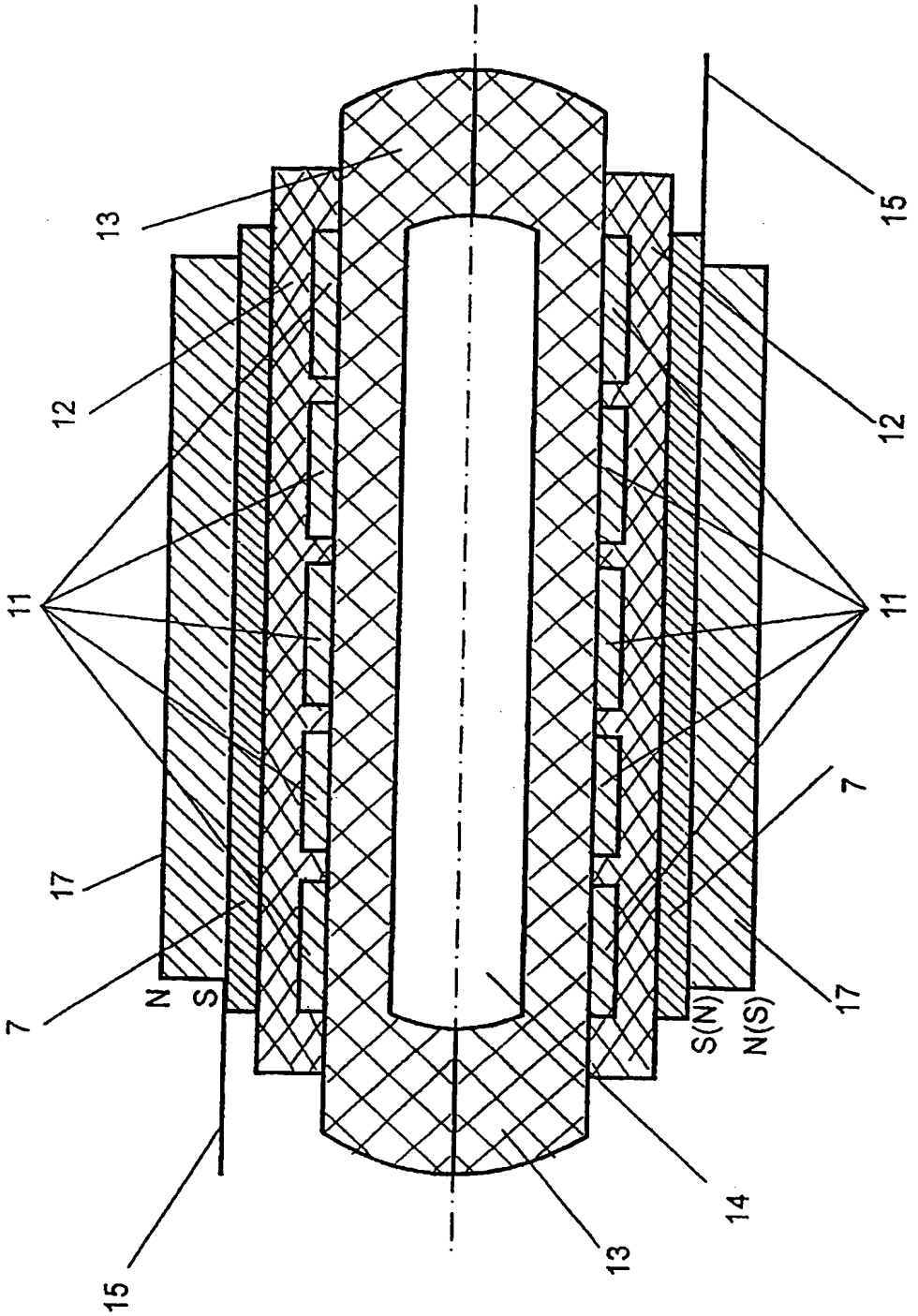

FIG.3

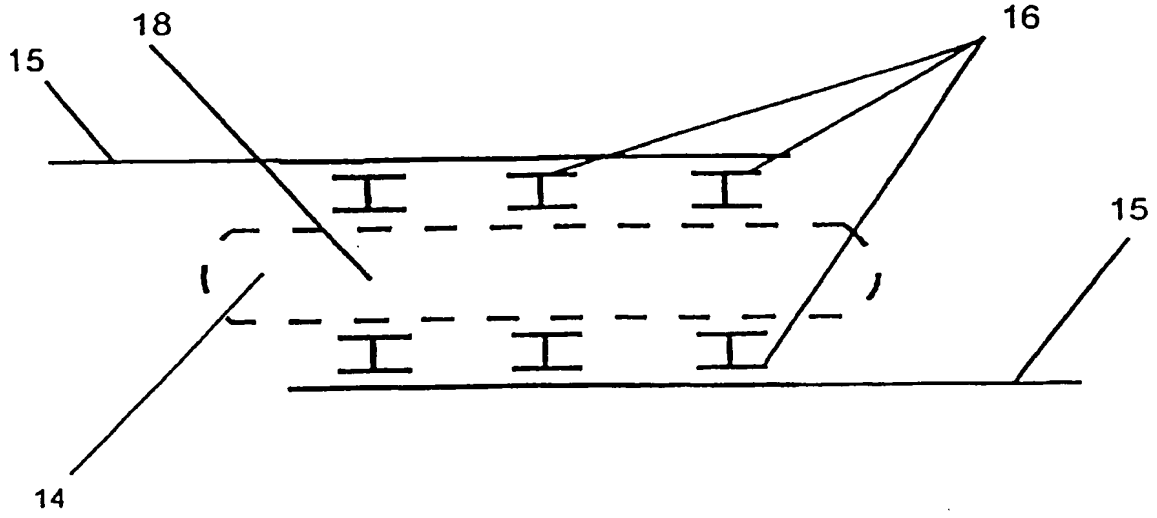

FIG.4

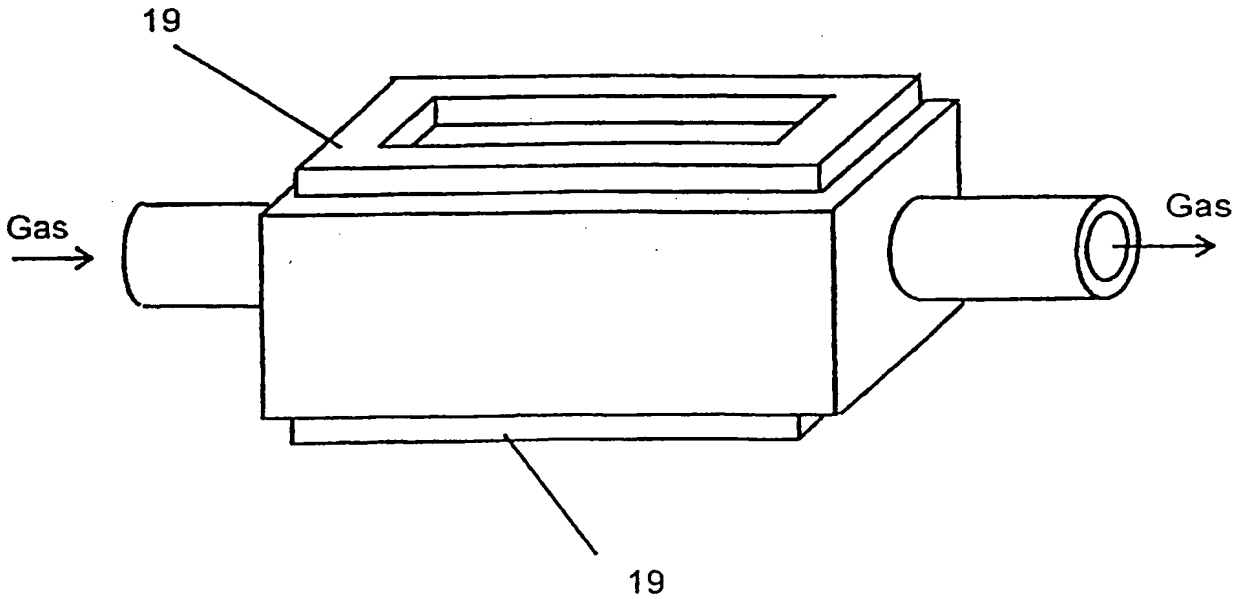

FIG.5

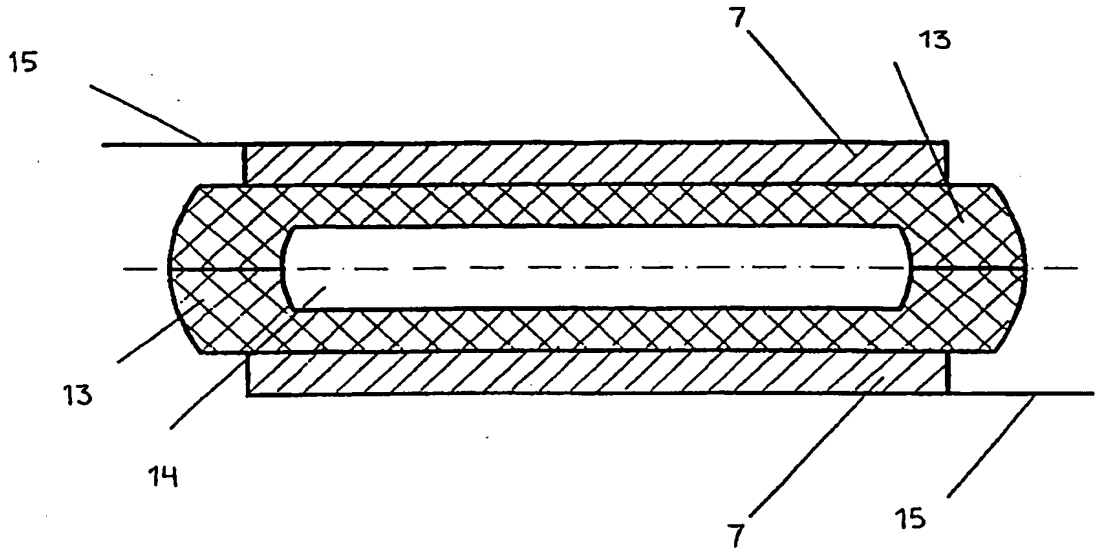

FIG.6

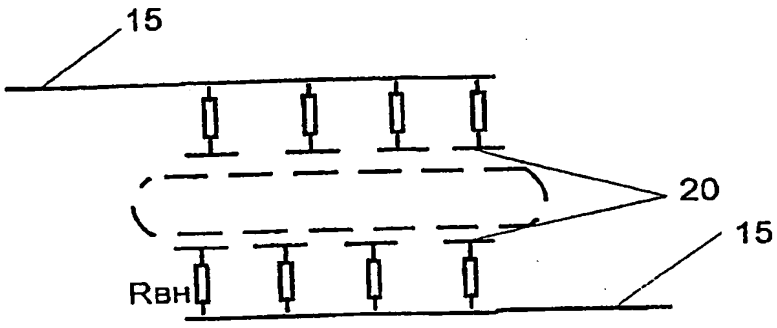

FIG.7

INTERNATIONAL SEARCH REPORT

In ational Application No
PCT/EP 99/01824

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/32 B01J19/08 H05H1/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D B01J H05H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 44 32 012 A (COMMISSARIAT ENERGIE ATOMIQUE) 23 March 1995 (1995-03-23) the whole document ---	1,8
Y	EP 0 825 692 A (HUGHES AIRCRAFT CO) 25 February 1998 (1998-02-25) the whole document & WO 98 07500 A (HE HOLDINGS INC) 28 February 1998 (1998-02-28) the whole document ---	1,8
Y	PATENT ABSTRACTS OF JAPAN vol. 095, no. 005, 30 June 1995 (1995-06-30) & JP 07 047223 A (MITSUBISHI HEAVY IND LTD), 21 February 1995 (1995-02-21) abstract ---	1,8
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
29 July 1999	05/08/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/01824

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 343 987 A (MITSUI TOATSU CHEMICALS) 29 November 1989 (1989-11-29) column 7, line 55 - column 8, line 65; figures 3,4	1,7,8, 25,26
A	WO 88 08325 A (WESTINGHOUSE ELECTRIC CORP) 3 November 1988 (1988-11-03) page 6, line 33 - page 11, line 15; figures 1-5	1,8, 16-21
A	EP 0 366 876 A (MITSUBISHI HEAVY IND LTD) 9 May 1990 (1990-05-09) claims; figures	1,8
A	WO 98 02233 A (BATTELLE MEMORIAL INSTITUTE) 22 January 1998 (1998-01-22) figures	1,8
A	DE 44 16 676 A (SIEMENS AG) 23 November 1995 (1995-11-23) the whole document	1,8

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ational Application No
PCT/EP 99/01824

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4432012 A	23-03-1995	FR 2709980 A	24-03-1995
EP 0825692 A	25-02-1998	US 5836154 A	17-11-1998
		JP 10156131 A	16-06-1998
		US 5906715 A	25-05-1999
JP 07047223 A	21-02-1995	NONE	
EP 0343987 A	29-11-1989	JP 1297126 A	30-11-1989
		US 4985213 A	15-01-1991
WO 8808325 A	03-11-1988	US 4818355 A	04-04-1989
		PT 87336 A,B	12-05-1989
EP 0366876 A	09-05-1990	JP 2115024 A	27-04-1990
		JP 2131123 A	18-05-1990
		AT 89187 T	15-05-1993
WO 9802233 A	22-01-1998	US 5914015 A	22-06-1999
DE 4416676 A	23-11-1995	WO 9531271 A	23-11-1995
		US 5746051 A	05-05-1998

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